

CARBONIZATION OF OIL-SHALE USING A
FLUIDIZED SOLIDS TECHNIQUE

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By

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Bachelor of Science

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Lubbock, Texas

1943

Submitted to the Department of Chemical Engineering

Oklahoma Agricultural and Mechanical College

In Partial Fulfillment of the Requirements

for the Degree of

MASTER OF SCIENCE

1949

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PREFACE

With a dwindling supply of known petroleum reserves, and an ever increasing demand for liquid fuels, the production of liquid fuels from other sources is a matter of paramount importance.

Oil-shales are a possible source from which liquids can be produced. This study deals with the feasibility of employing a fluidized technique to the retorting of oil-shales.

ACKNOWLEDGEMENT

The author wishes to take this opportunity to thank all of the members of the Chemical Engineering Staff at Oklahoma A & M College for their continued interest and encouragements.

Thanks are due especially to Dr. W. A. Klemm, who supervised this work.

The author's interest in this problem had been stimulated by his short experience at the Bureau of Mines Oil-Shale Demonstration Plant at Rifle, Colorado.

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INTRODUCTION AND LITERATURE SURVEY

A very large potential reserve of liquid fuels exists in the United States and many other parts of the world in the form of oil-shales. These shales vary widely in character and organic content. A property common to all shales is the insolubility of their organic material in conventional solvents (including shale oil). Thermal decomposition is the only way in which the solid organic material can be directly converted into liquid products. Much work has been done on the mining and retorting of shales together with the recovery and utilization of the products. The most important current work is being carried out by the United States Department of Interior, Bureau of Mines.

In general, carbonization products are similar to both petroleum and coal tar, having properties somewhat intermediate between the two. As in the case of coal tar, rate of heating, temperature of retorting, and degree of "cracking" have considerable influence on the products. The solid product of low temperature carbonization of a typical oil-shale is about 5% free coke and 95% impure argillaceous limestone containing iron, magnesium, and silica. (If high temperatures are employed, the mineral carbonates also decompose.) About 28^{*} gallons of oil and 900 cu. ft. of gas having a heating value of from 800 to 900 Btu./standard cubic foot are produced from a ton of raw shale. Many processes using broken shale have been attempted with varying degrees of success. The chief difficulties to be overcome are low heat transfer rates to packed beds, channeling, materials handling, difficulties in maintaining pressure seals with continuous feed of solids, poor heat utilization, and dilution of products. Approximately 300 Btu./lb. of shale are required to fur-

* This figure varies from 5 to 90, but the 28 gallon per ton shale seems to be the most likely to be worked.

nish the heat necessary to retort the shale at 800° F. (this includes latent and sensible heats.) As in the case of coal, no accurate data are available. The reaction could be exothermic.

Conventional retorts may be classified under three categories:

1. In the gas producer type a counter current sequence of combustion and carbonization is carried out. The advantages of this method are adiabatic and counter current operation. The character of American shales does not permit the use of pure air because of caking caused by the fusion of the inorganic material present in the shale. Thus, a recycle of inert gas is necessary, further diluting the product. Also, considerable heat is wasted in decomposing the mineral carbonates (which results in more dilution). The vented gas is in the form of mist, and has a negligible heating value. While it is possible to make such a process intermittent, the mechanical obstacles are many, the capacity is low, and complete recovery of the products (especially the light ends) is difficult.
2. A bed of broken solids can be heated through the walls. From reading the discussion in reference # 1., it is not clearly understood why this type of retort has not been given further consideration in the treatment of American shales. Apparently, caking and channeling occurred, and the total yields of liquids were adversely affected due to the high temperatures. The single retort investigated was not self sufficient in fuel gas because of heat losses. Such retorts have been used in Scotland, where, in the absence of native petroleum, the oil-shale industry has managed to survive. It was found that the capacity of such retorts could be markedly

increased (to about six tons per day) by blowing steam through the charge at slow rates. Steam also tends to produce higher ammonia yields. This has not been found true of American shales or coals.

3. In another type, circulating gases are externally heated. This method has practically the same disadvantages of the internal combustion type, inasmuch as gases have relatively low heat capacity. By recirculating the gases before removing the light ends, perhaps the dilution with respect to these fractions could be minimized if adverse cracking did not occur while being heated.

The magnitude of the disadvantages entailed in these types together with mining problems (and remoteness of location in the U.S.A.) may be better comprehended if it is noted that although oil-shales have been known and studied for more than half a century, no commercial oil-shale industry has ever thrived. The Scottish industry alone has eked out a survival. This has been done by re-tailing many products and by manufacturing by-products such as bricks and fertilizer.

In all types (except the high temperature) fines must be rejected to minimize channeling.

A tremendously potent process tool known as fluidization is currently undergoing intensive development. While as yet only one type of large scale industrial process* utilizes the full advantages of the method, the manifold advantages inherent in such a system strongly indicate its further, varied industrial applications.

It has been observed that gas flowing upward through a column of finely

* Catalytic cracking of petroleum.

divided solids causes an apparent expansion of the solid bed and that, within certain velocity limits, the mixture resembles a boiling liquid. There is extreme turbulence and agitation, and the mixture has many properties of a fluid. Parent⁷ maintains that void or pore gas velocity necessary to induce a turbulent condition is less than the free falling velocity of the smallest sized particles, if calculated assuming a spherical shape. The density of the fluidized bed can be controlled by adjusting the relative velocity of the aeration gas.

The advantages of such a system are listed below:

1. Tremendous mass throughputs are feasible. For clay moving upward a mass throughput of 4000 pounds per minute per square foot is possible.³ This is 2880 tons per day per square foot.
2. Pumping efficiencies as high as 65% are obtainable.³
3. By adjusting densities and heights, material can be made to flow from one vessel to another under the influence of hydrostatic head. Data published on one catalytic cracking unit indicate that 13,000 tons per day of catalyst are circulated in this manner.⁹ This unit was designed for minimum catalyst circulation.
4. An extremely uniform temperature distribution within the fluid bed has been observed. The fluid bed acts as a thermal flywheel and lends itself to ready and exact temperature control. Local overheating is eliminated, hence undesirable side reactions may often be minimized. A temperature variation of less than 5°F. has been observed in adiabatic catalytic cracking units.*

* W. K. Lewis, personal communication.

5. The lowest possible reaction temperature may be employed because of the very rapid reaction rates attainable for a gas-solid reaction. No matter what the nature of the reaction, all other factors being equal, the reaction rate is directly proportional to the surface exposed.⁸ The surface per unit mass is inversely proportional to particle size.
6. High coefficients of heat transfer - of the order of those obtained to boiling liquids - have been reported. No actual data have been published on this phase. Parent⁷ reported only a 5% increase to a 3% decrease in the overall coefficient from condensing steam to nitrogen when suspended solids were present, over that overall coefficient obtained when the solids were absent. However, no numerical values were given, and the discussion was not detailed enough for a reader to evaluate the data or decide whether or not the data are as contradictory with the statements of others as they would seem to be at first glance. An answer to a question regarding the coefficient of heat transfer from "fluid" to boiling water in a catalytic cracker regenerating unit was that the observed overall coefficient was "about 25".⁵ The authors of a more recent article² maintain that, by using a fluidized technique, only 0.5% as much heat transfer surface is necessary to remove the heat generated when producing 10,000 Bbl/day of liquids by a Fischer-Tropsch Synthesis as was required by a German plant employing packed tube reactors. Meyer⁴ reports that the coefficients from a steam heated wall to air can be doubled when solids are present. It was reported that Nicholson⁶ gave a figure of 300 for the heat transfer coefficient from a wall to a fluid bed in the temperature range of 800° F.

7. Any gas or vapor which does not form undesirable reaction products may be employed as an aerating medium.
8. Almost any size material may be fluidized, but, with larger sizes, the advantages are diminished.
9. Smoother mechanical operations with fewer equipment shut downs are usually possible.

Some properties may be either advantageous or undesirable:

1. The great turbulence tends to produce a uniform bed of material at equilibrium. This precludes counter current action (with respect to solid) within a single fluid bed. The solid product withdrawn is of essentially the same composition as the reacting mass. The gaseous reactants may be purged by an aerating gas or vapor when the solids are in transit from one reactor to another.
2. With wide variations in particle sizes, some segregation is effected. The fines have a greater tendency to be carried overhead; this effect increases with greater gas velocities.

Some disadvantages entailed are:

1. The comminution cost (if the solid is to be reacted). Crushing and grinding of thousands of tons per day of mineral ores is being accomplished at surprisingly low unit costs.* With proper design of even small units, handling one hundred tons per day could be possible at costs which would probably not be prohibitive, especially in view of the process savings encountered elsewhere.
2. Difficulties in laboratory scale investigations. Due to wall effects, irregular behavior is observed in reactors of less than

* Various Bureau of Mines publications on specific mills.

two inch diameter. Above four inches, the diameter seems to have little effect. Batch type reactors do not reliably predict performance of a continuous unit and continuous systems are difficult on a laboratory scale.

3. Limitations of gas velocities. If a "fixed" reactant bed is employed, low gas velocities are necessary to avoid appreciable carry over of the solids. Valuable solids such as catalysts can largely be recovered, but economic losses are sustained both as replacement and recovery costs. If the products are gaseous, it is usually desirable to remove the dust, although the value of the solid might not warrant its recovery. This limiting gas velocity necessitates the use of reactors with large cross sectional areas.
4. Erosion of walls, especially in bends.

If such a system could be applied to oil-shales, a wide variety of continuous flow patterns could be used.

There is a strong possibility that enough gas could be generated to supply all the heat necessary for retorting, in which case an externally heated retort with the solids simply being discarded could be used. Maximum yields of desirable oil fractions might eliminate this.

If the heat transfer coefficients are as high as reported, and, if better utilization of the gas (such as synthesis gas production) can be found, it would seem that a simple flow pattern could be one in which the shale were retorted in one vessel and the residual carbon burned in another vessel surrounding or surrounded by the first.

Meyer⁴ points out that, although the heat transfer coefficient from a steam heated wall to a gas can be doubled by the presence of fluidized solids, it is possible to obtain higher heat transfer coefficients in conventional gas

heat exchangers for the same pressure drop. This would probably not be true at higher temperatures, where radiation is important. The advantages to be gained in heating the fluidized mixture would not only be higher heat transfer coefficients, but lower temperature levels and less gas circulation (dilution).

There can be little doubt that the residue of carbonized shale containing 5% carbon could be burned with air in a fluid bed, since the catalytic cracking regenerators are fed material containing only 3% carbon.⁹ Decomposition of the carbonates will probably limit the temperatures attainable.

Pulverizing the shale will be an item of major cost, although crushing presents little difficulty. Moreover, a savings could be realized over broken solids methods in the utilization of the fines, which would normally be rejected. For high capacity with minimum maintenance, ball mills or rod mills with "air classification" using flue gas could be used. Hammer mills could prove satisfactory, although these are seldom used in large scale mills.

Considering the choice of an aerating gas for the carbonization zone, it would be desirable to employ a condensible vapor such as steam which would minimize the dilution of the light ends.

At retorting temperatures the decomposition of steam would be negligible. Another possibility would be to recycle the gas prior to the collection of the light ends. In this case the light ends would be subjected only to retorting temperatures and not to stove temperatures.

Saturated hydrocarbon vapors might also be used and could possibly improve the product.

Minimum quantities of aerating gas should help promote film-wise condensation, in lieu of mist formation. Complete removal of dust and selective condensation of products would also minimize mist and emulsion formation.

A major objection to the possible application of fluidization is agglomeration. Like coal, shale is reported to soften when heated. Wang¹¹ reported that only 0.6% by weight per minute of coal could be fed into a fluidized bed of coke at carbonizing temperatures. This would eliminate a commercial application. Singh⁸ reported success in his experiments on the partial devolatilization of coal using an overhead carry over.

A study of the problems encountered to develop such a system would include systematic investigations of:

- (a) Fluidized flow characteristics of raw shale and retorted shale.
- (b) Heat transfer coefficients to fluidized solids at various temperature levels.
- (c) Studies of the heat requirements to retort shale under various conditions.
- (d) Combustion studies of carbonized shales in dense and light phase fluidization.
- (e) Combination of combustion and carbonization flow patterns.

It would be well beyond the scope of this thesis to attempt complete studies of any of the above categories. Moreover, a step must be taken to determine whether or not a fluidized technique can be applied at all before the above studies would be worthwhile. Since Wang¹¹ reported agglomeration of batch processes, even when only 10% coal was used with coke, continuous flow and steady state conditions will be prime objectives.

It is therefore intended to determine under what condition shale can be carbonized, that is, even if coking occurs in a fluidized bed, conceivably plugging could be avoided by adjusting flow rates, temperature, direction of flow of gas and solids, concentration of solids, rapidity of heating and other minor factors.

If successful fluidization can be achieved, it would be desirable to obtain as much data as possible (oil yields, etc.).

PURPOSE

The purpose of this work was to investigate the feasibility of applying a fluidized solids technique to the carbonization of oil-shale, and to build and operate a laboratory scale retort.

PROCEDURE

A. Exploratory experiments in fluidization.

The published literature gave very little information as to actual techniques employed in handling fluidized solids. The first step was to observe Filtrol suspended in air.

It was possible to take a thief sample of the mixture. When fluidized at low air rates, the flow of solids appeared to be up at the center and down at the walls. There was a constant washing action of the solids on the walls.

When powdered coal was dropped in the top, the mass instantly became uniformly gray with high gas velocities; at lower gas velocities, black streaks folded down the walls becoming lighter and finally merging into the gray mass.

Cotton wads were stuffed into the top of the tubes to prevent dusting, but these were always quickly plugged and either blew out or stopped gas flow.

The rate of dusting seemed to be fairly constant at any one velocity. Presumably a run could have been made long enough to carry out all the particles smaller than a definite size, but this was not attempted.

Some particles were carried out of the bed for quite a distance but dropped down again.

Dust collected on the top edge and on both the inside and outside tube walls. The inner wall was maintained clean by the washing action of the solids, but heavy dust deposits accumulated above the upper level of the bed.

There was a greater tendency to slug (piston action) in small tubes, especially when solids were added before the air was turned on.

Several attempts were made to feed solids continuously through a standpipe to a fluidized bed using standard pipes and fittings without success. The exact actions were not observed, but the results were that the gas selectively channeled through one pipe, usually suddenly blowing the contents out. Even though separate gas feeds were used to two pipes connected by a horizontal nipple of the same diameter ($1\frac{1}{2}$ "), channeling would occur through the nipple so that the contents of the bed above the nipple would be carried overhead. Sometimes the contents of the other pipe would fall and sometimes packing resulted. Addition of solids to one of two pipes connected by a small diameter pipe through which air was fed would result in a fluid bed in both, but attempts to add solids to one side often resulted in selective flow through the other. A crudely fashioned slide valve, with the standpipe aeration supplied through a vertical glass tube above the valve, was tried. This valve was rendered inoperable by solids wedging in the sliding parts.

Filtrol in small tubes $1/4$ - $5/8$ inches would sometimes flow out evenly and sometimes pack. None would flow from a large separatory funnel with or without aeration. There seemed to be two entirely different types of flow. One resembled closely a flow of uniformly sized grains in an

hour glass. The other resembled a liquid flow in which no solid could fall unless a gas bubble displaced it. In the former case, the gas probably channeled as it would through a packed column.

B. Qualitative experiments with powdered shale and coal.

A porcelain crucible was placed in the top of a Hoskins furnace and the crucible filled with powdered shale. This was stirred with a looped iron wire in an effort to maintain uniform temperatures. Only very slight local grain growth appeared as the shale began to evolve gases. The gas and fume evolution lasted for some time with a blackened residue remaining. When stirring was ceased, the shale became fairly quiescent with only a few gas "bubbles" being formed and broken. (The surface became speckled white due to combustion). Stirring was resumed and a small quantity of raw shale was added. Gas evolution was fairly rapid but not instantaneous. No agglomeration was apparent.

A small quantity of coal was added and a disproportionate amount of clinker was formed in the shale. Nine other standard coal samples were tried. Of the ten, only three agglomerated when added to either coke or carbonized shale. Proximate analyses and sulfur contents revealed no correlation except that the high volatile coals with low moisture contents would not. Later, the moisture was found to have been correlated with other properties - including coking and agglutinating value. Only the coking coals agglomerated and these did not when pre-mixed with oil-shale.

When a test tube filled with powdered shale was heated in the furnace, a fused mass, which could not be probed, was formed. This was obviously a mixture of retorted shale on the sides with layers of tar and shale toward the center.

A 50 gram sample of raw shale was then jiggled with nitrogen in a

small glass tube and heated in a furnace. Copious volumes of fume and soot were evolved. When the nitrogen rate was decreased slightly, some hot shale dropped down through the inlet tubing and ignited the rubber stopper. Plugging did not occur but slugging did. The discharged solids were uniformly black. Some tar and raw shale dust stuck to the upper inside (unheated) section of the tube.

C. Continuous Operations.

A series of runs was made with so many factors changed from one run to the next that only qualitative results were obtainable. The first feed system tried was a rubber stopper plunger type. It was hoped that the rod could be used to overcome the packing tendencies. However, selective channeling occurred and the pressure built up when the upper stopper was closed (or the hopper charge was blown out). Sometimes the feed line would clear, but, more often, it would not. Flow of solids was blocked at every possible point at one time or another.

Using the same piping but a flask hopper and a modified gate valve, a detachable hopper was tried. At high gas velocities this could feed very rapidly, but it was difficult to initiate flow of solids after refilling, and it was impossible to regulate the feed or to take data while manipulating the feeder.

Velocities necessary to feed the solids were too high to maintain the fines in the retort.

Most of the feed difficulties were found to have been due to the horizontal section of piping connecting the feed entrance with the bottom cone and to the bends. Bad channeling occurred in a horizontal or inclined pipe, and the larger solids collected at bends, blocking flow altogether.

Coarse material (+ 35 mesh) could be dropped out the bottom of the

cone by an immeasurable decrease in velocity, apparently at a constant rate.

Considerable time was spent trying to mount and drive a screw conveyor, which worked when turned by hand, but was not pressure tight and could not be driven in place by the motor used without binding.

Gravity feed at an angle of about 30° with the vertical tube was tried. Although the effective entrance area could be increased by the angle cut, even a $5/16$ -inch tube could not be used to feed a $1/4$ -inch tube. An equal or smaller diameter could be used. A feed point of $1/4$ -inch pipe was made and used in two runs. One-eighth inch pipe was used in the remaining runs. A standpipe could be operated either opened or closed at the top. Unless channeling occurred, the feed rate would be uniform. When channeling occurred, and the standpipe contents became aerated, the feed rate increased until channeling became so great that the contents of the standpipe were blown overhead.

Logs of the later runs are included in Appendix I.

No quantitative data were obtained from these runs since plugging in the gas take-off line always occurred.

D. Batch Operations.

There were so many possible factors which could have caused the plugging such as polymerization, condensation due to cooling, solid carry over (slugging), attrition and decrepitation of solids, and channeling of the feed that it was decided to build a batch retort to obtain quantitative data.

Eleven runs were made, each using a 650 gram charge and nitrogen rate of 0.3 standard cubic feet per minute (corresponding to a linear velocity of 0.25 feet per second at 90° F. and to a velocity of 0.87 feet

per second at 1100°F). This velocity was sufficient to fluidize the material in a 2-inch pipe and prevent any of the charge from falling through the 1/8-inch pipe.

Operational steps:

1. Nitrogen pressure was adjusted to 26 psig. with the flow meter reading 4.5" H₂O.
2. A 650 gram charge of raw shale was dumped into the retort through a funnel and a two foot length of 1/2-inch pipe.
3. The thermocouple shield and asbestos plug were inserted.
4. Initial thermocouple readings were taken.
5. Heaters and clock were turned on.
6. Readings were taken at two minute intervals. Each set of readings required from 1/2 to 1 minute.
7. Rheostats were adjusted and heaters turned on and off in attempts to maintain the upper wall temperature equal to the bed temperature.
8. When discharging, the heaters and gas were turned off; the cork was removed from the bottom nipple; and the solids allowed to flow into a 1000 ml. round-bottom flask. The flask was supported by pipe insulation in a position so that the 3/4-inch nipple extended two inches below the mouth of the flask. The flask was then stoppered and allowed to cool. The nipple was corked up and the retort allowed to cool. When cool, the retort was examined.
9. The solid discharge was weighed. A sample was taken by random spoonfuls when pouring from one can to another repeatedly. The bulk of the discharge was then mechanically

screened for one hour.

10. Ash determinations were made by ignition at 1800°F for twelve hours.
11. Inorganic volatile matter was determined volumetrically by acid liberation and pipette absorption. It was arbitrarily assumed to be CO₂ for weight conversion, although some H₂S was known to have been liberated.

Tabular data and a distillation curve are included.

Logs of the runs are included in Appendix II.

APPARATUS

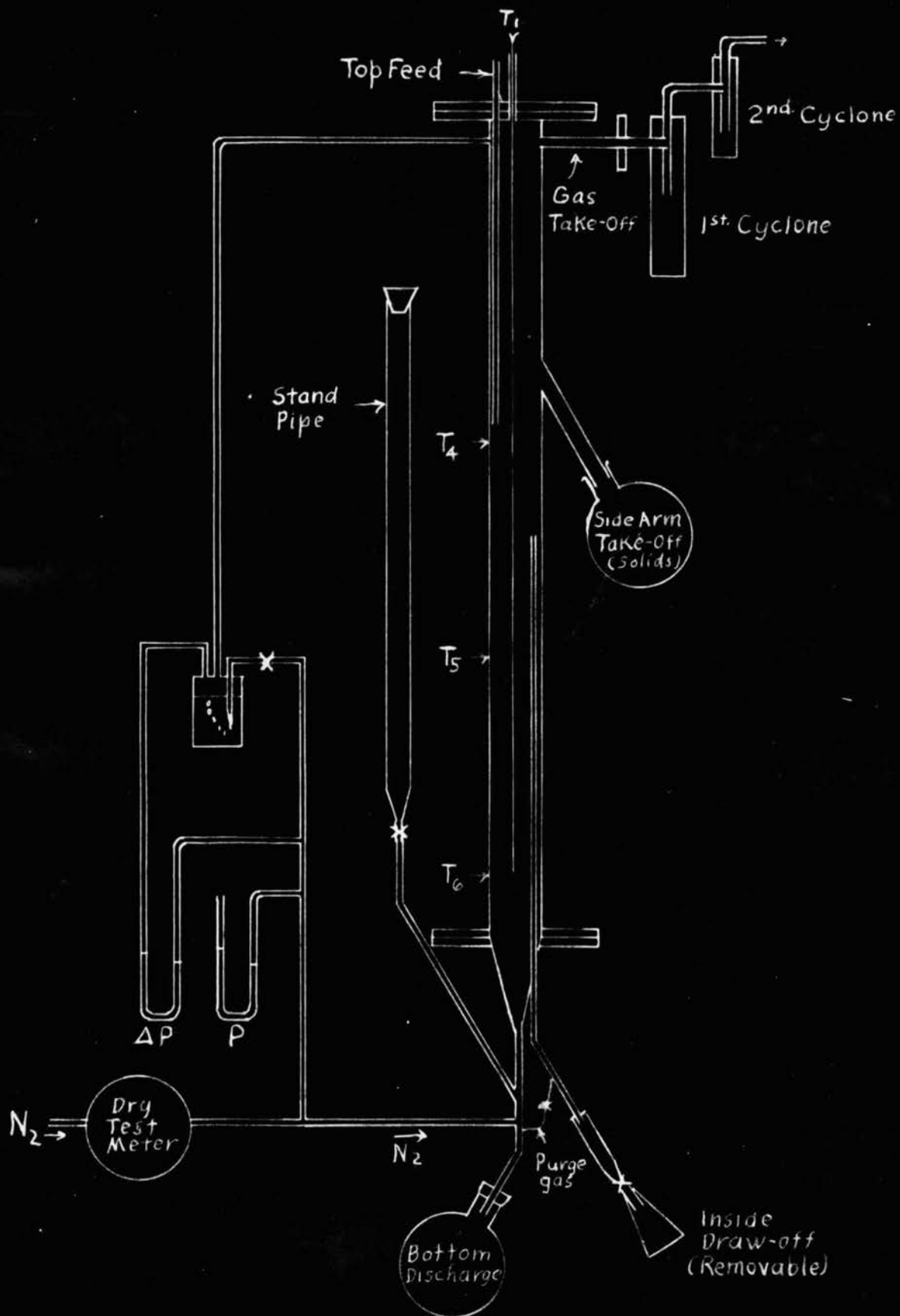
A. Continuous Retort.

The retort (see Sketch 1.) was constructed from a 30-inch length of standard (schedule 40) black pipe. Flanges at the top and bottom were cut from 1/2-inch boiler plate. The conical section was rolled from 22-gauge sheet metal and brazed. The taper of the cone was 1/6. Asbestos gaskets were used at flanged joints.

The retort was supported on a single upright by strips of steel which were welded to the flanges at the top and bottom. These strips were bolted to the flattened ends of 3/4-inch nipples. The nipples were screw-fitted to tees. The tees, which were movable along the upright, were held in position by set screws.

The gas take-off was 1/4-inch pipe. The side arm take-off was of 3/4-inch pipe welded at an angle of 30° with the vertical. Pressure taps were of 1/8-inch pipe. The upper nine inches of the bottom take-off was an open end 1/8-inch pipe welded to a 1/4-inch pipe, which was continued through the cone. The screw clamp on the rubber tubing was closed when

FIGURE 1.
CONTINUOUS RETORT



replacing the flask which was used to collect the solids being discharged.

The standpipe was a 3/4-inch glass tube marked at 10 gram intervals. A 500 ml. volumetric flask was sometimes used as a feed hopper in lieu of the standpipe.

Wall thermocouples were placed in circumferential grooves in the pipe wall and the half-turn, which was remote from the junction, was insulated from the metal by one layer of asbestos paper. The center thermocouples were unshielded. Porcelain insulators were used. "Spiders" for centering the thermocouple were made of twisted nichrome wire.

Three 500 watt windings of #22 nichrome wire were used to heat the lower 20-inch section. A single 200 watt winding was used for the upper 10-inch section and a 500 watt winding was distributed between the two cyclones. Two thicknesses of asbestocel pipe insulation were used on the retort, and a single thickness was used on each of the cyclones.

A dry test meter was used to meter the aerating gas. Temperatures were measured with a potentiometer type instrument which was calibrated in degrees Fahrenheit and contained an internal cold junction compensator. Thermocouples and leads were made of chromel-alumel. Single throw, double pole, switches were used to close the desired thermocouple circuits.

B. Batch Retort.

This retort (Sketch 2.) was constructed from a four-foot length of 2-inch pipe. The cone was rolled from 14-gauge sheet metal and welded. The taper of the cone was 1/6.

One 1200 watt winding of #14-gauge nichrome wire was used to heat the upper three foot section, and a single 1000 watt winding was used to heat the conical section and the lower 12 inches of the 2-inch pipe.

Three layers of asbestos paper were used for electrical insulation

between the windings and the metal wall.

Provisions were made to heat the entering gas (to increase linear velocity), but this expedient was found to be unnecessary.

Two thicknesses of pipe insulation were used on the retort. The insulation was extended down 6-inches below the bottom of the cone. The space between the cone and the cylindrical pipe insulation was filled with asbestos cement. The relatively flat bottom formed in this manner was supported by a flat cast iron ring on a tripod.

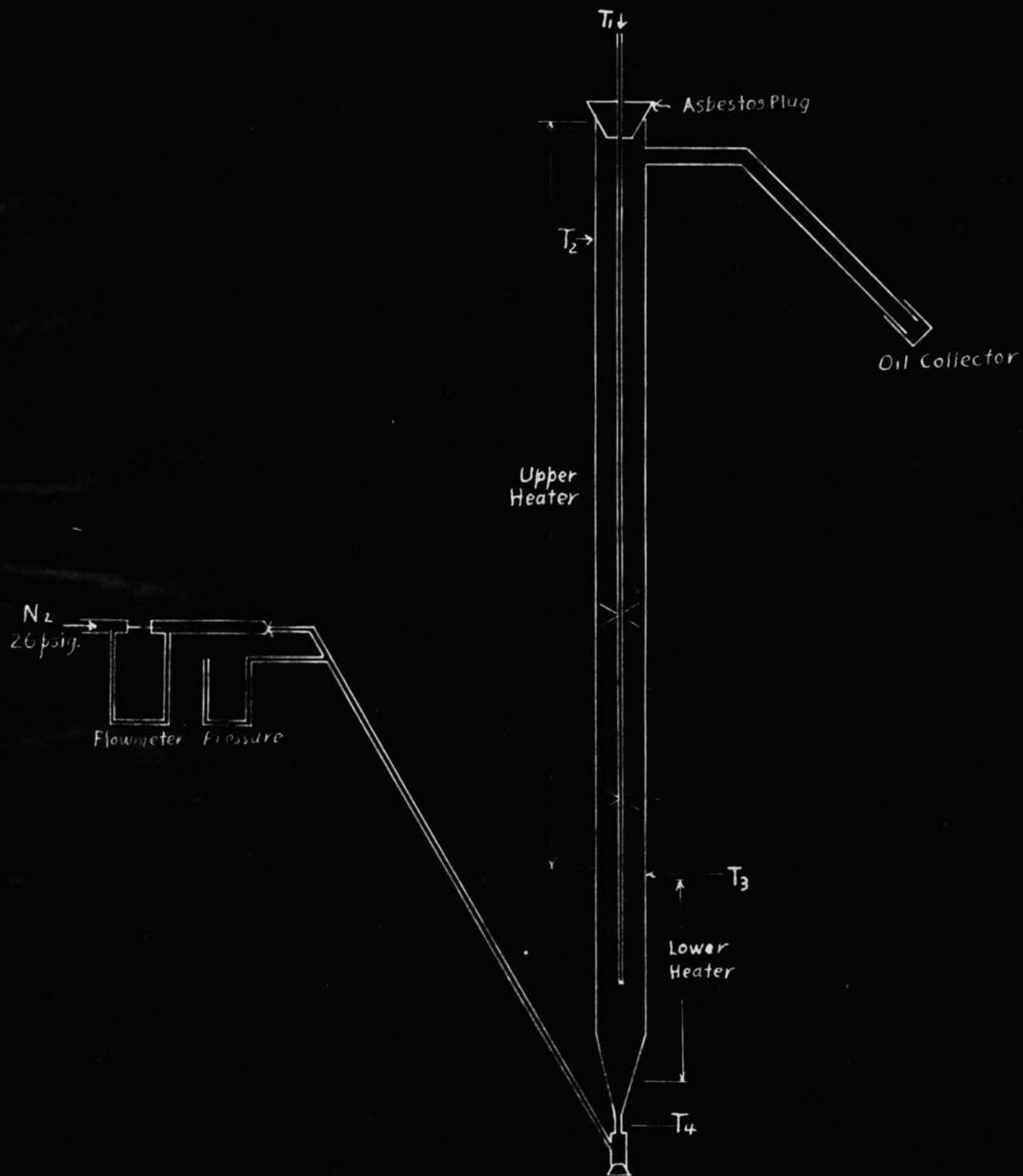
Horizontal support was effected by looping the #10 single strand copper wires (lead wires to heaters) around both the outside of the insulation and the upright.

One wall thermocouple was placed 36-inches above the top of the cone. Another thermocouple was placed 12-inches above the cone (between the upper and lower windings). A third thermocouple was placed 1/2-inch below the inlet to the cone -- along the 1/8-inch pipe. The same manner of installation as previously described was used.

A thermocouple shield of 3/16-inch stainless steel tubing was used. "Spiders" of 1/16-inch welding rod were placed at points 14-inches and 26-inches above the bottom. The shield was supported by an asbestos cement plug at the top of the retort.

The gas take-off was a 3/4-inch standard pipe 4 inches long and threaded on one end. This was welded horizontally at a point 4 inches below the top of the retort. To this nipple, a pipe coupling, a short nipple, a 45° elbow, and 2 1/2 feet length of 3/4-inch pipe were connected in order to vent the gases to the atmosphere. After it was observed that liquids were being condensed in this line, a tin can was wired on the end of the pipe to collect the liquid.

FIGURE 2.
BATCH RETORT



RESULTS

The results are tabulated in Tables I and II. The distillation curve which was obtained is plotted in Figure 3.

Logs of the last few continuous runs are included as Tables III, IV, and V in the Appendix.

The logs of the batch runs are included in the Appendix as Tables VI through XV.

It should be noted that the shale herein investigated contained a potential yield of 26 gallons per ton of oil and 5 gallons per ton of water as determined by the Fischer Assay Retort.* These figures correspond to 10% and 2% by weight, respectively, of the raw shale. (Only 0.3% by weight is free water.)

When a fluidized bed of oil-shale was heated at a rate such as is shown in the typical heating curve for Run 4B (Figure 4), dusting and decomposition began almost at once. As the temperature was increased, the gas became more opaque.

While the discharged gas was visible at 550° F, this was due almost entirely to dust and steam. When held at 550° F for an hour (Run 7B, Table VIII), only 1.4% of the shale distilled.

When the shale was heated to 750° F (Run 1B, Table VII), 2.3% of the shale distilled. The gas did not become yellow; the solids were fuming slightly when they were discharged and the solids were only slightly darkened. Only a trace of oil agglomerated with the dust which had collected in the gas take-off.

* Bureau of Mines Oil-Shale Demonstration Plant, Rifle, Colorado — Personal Communication.

When held at 750° F for one hour (Run 2B, Table VIII), 8.5% of the shale distilled. This is equivalent to a distillation rate of 6.2% per hour at 750° F. Although the gas was yellow, only a negligible amount of oil was collected.

During Run 3B (Table IX), the shale was heated to 800° F and 7.6% of the shale distilled. Only 0.9% more was distilled by holding the shale at 750° F for one hour as was distilled in the time interval of seven minutes between 750° and 800° F. Moreover, liquid oil was collected during this interval, further demonstrating that the reactions were more rapid at the higher temperatures. The discharged solids were fuming.

Run 4B (Table X) was made by holding the shale at 800° F for one hour. A total of 13.0% of the shale distilled under these conditions. That is, 5.4% were distilled at 800° F within one hour. However, the gas remained yellow for only 20 minutes during this time so that the actual rate was probably three times as fast as the other data show.

Run 5B (Table XI) was conducted by heating the shale to 900° F. Under these conditions, 13.4% of the shale distilled. The gas was yellow for only the ten minutes between 760° F and 900° F. When the shale was held at 900° F for one hour (Run 8B, Table XIV), no further distillation took place. When the shale was inadvertently overheated to 940° F and held at 900° F for one hour (Run 6B, Table XII), only 13.7% was distilled.

For the final run (Run 9B, Table XV), the shale was heated to 1100° F and held for one hour. These conditions resulted in a distillation loss of 15.6%.

It is probable that the curve depicting the one hour distillation points (Figure 3) undergoes a sharp curvature in the neighborhood of 800° F. rather than the pronounced break which is shown.

Table I

BATCH RUN MATERIAL BALANCES

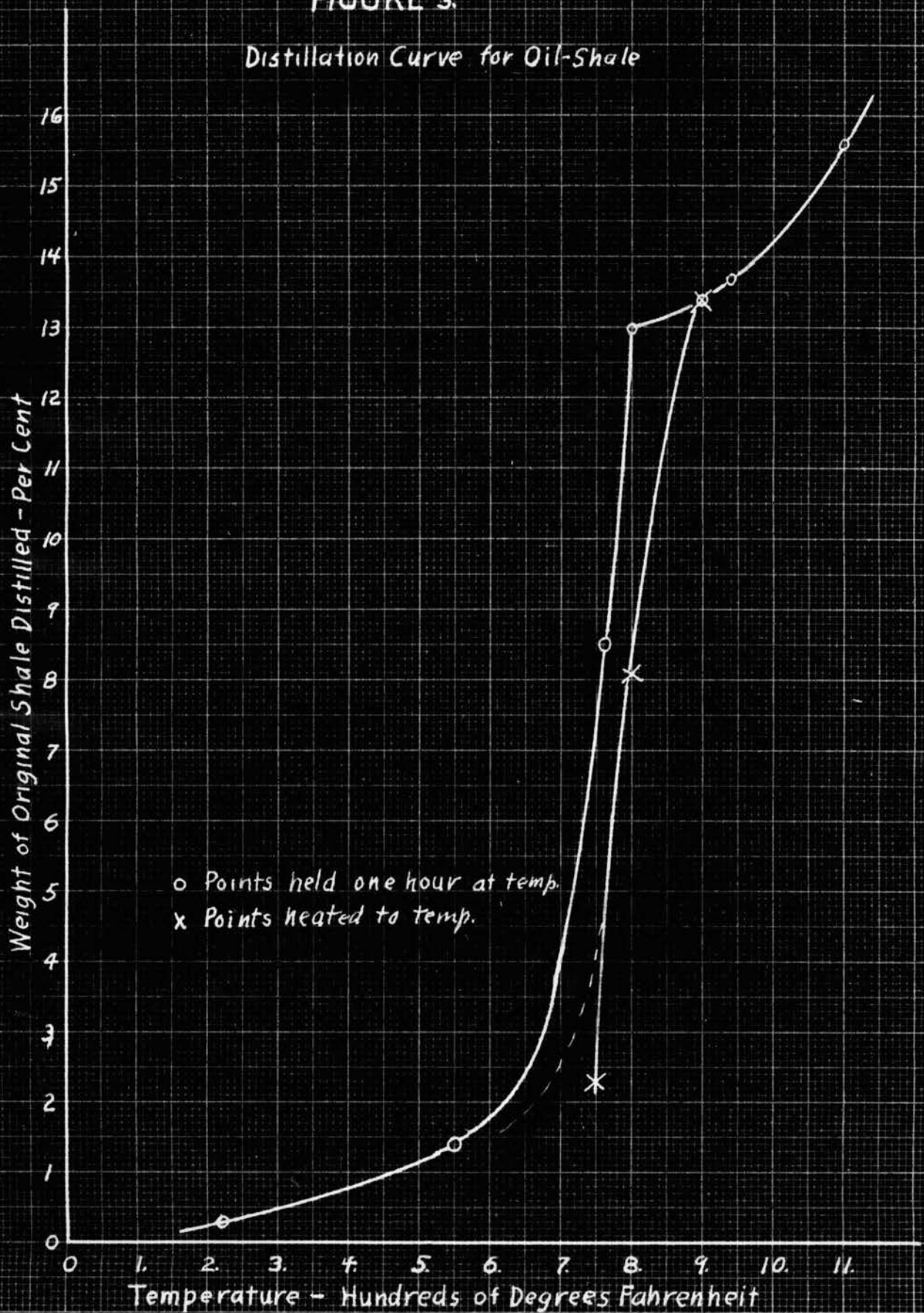
1. Run No.		7B	1B	2B	3B	4B	5B	8B	6B	9B
2. Temp. Attained, °F		550	750	750	800	800	900	900	940	1100
3. Time to heat (min.)		16	31	38	35	32	48	58	49	62
4. Time held at Temp. (min.)		60	0	60	0	60	0	60	60*	60
5. Total Overhead		3.7	3.8	11.4	12.1	17.2	17.2	18.8	19.3	21.2
6. VCM Overhead		2.3	2.7	9.4	9.2	14.4	14.4	15.0	15.2	17.1
7. Ash Overhead		1.4	1.1	2.0	2.9	2.8	2.8	3.8	4.1	4.1
8. Oil Collected	Per cent	0	nil	nil	1	2.3	3.5	3.4	3.4	3.4
9. Mud or Coke	of	1	nil	1	1	1.5	3	4	4	2
0. VCM Distilled	Original	1.4	2.3	8.5	7.6	13.0	13.4	13.7	13.7	15.6
1. VCM Remaining	Charge	35.0	34.1	27.9	28.8	23.4	23.0	23.0	22.7	20.8
2. CO ₂ Remaining		**	**	17	17	18	18	18	18	16
3. HC Remaining		**	**	11	12	5	5	5	5	5

* Held at 900° F.

** It was not possible to obtain reasonable duplications in analyses since shale was not wetted by acid.

NOTE: The term VCM is used here to denote material either volatile or combustible at 1800° F and hence, includes free and combined water and CO₂. Moisture determinations were made only on raw shale (0.3%).

FIGURE 3.
Distillation Curve for Oil-Shale



o Points held one hour at temp.
x Points heated to temp.

REPORT 2-1958-200
10 X 10 to the 1/4 inch, 5th lines omitted.
Sizing 8 X 10 in.
MADE IN U.S.A.

FIGURE 4.

Typical Heating Curve - Run 4B

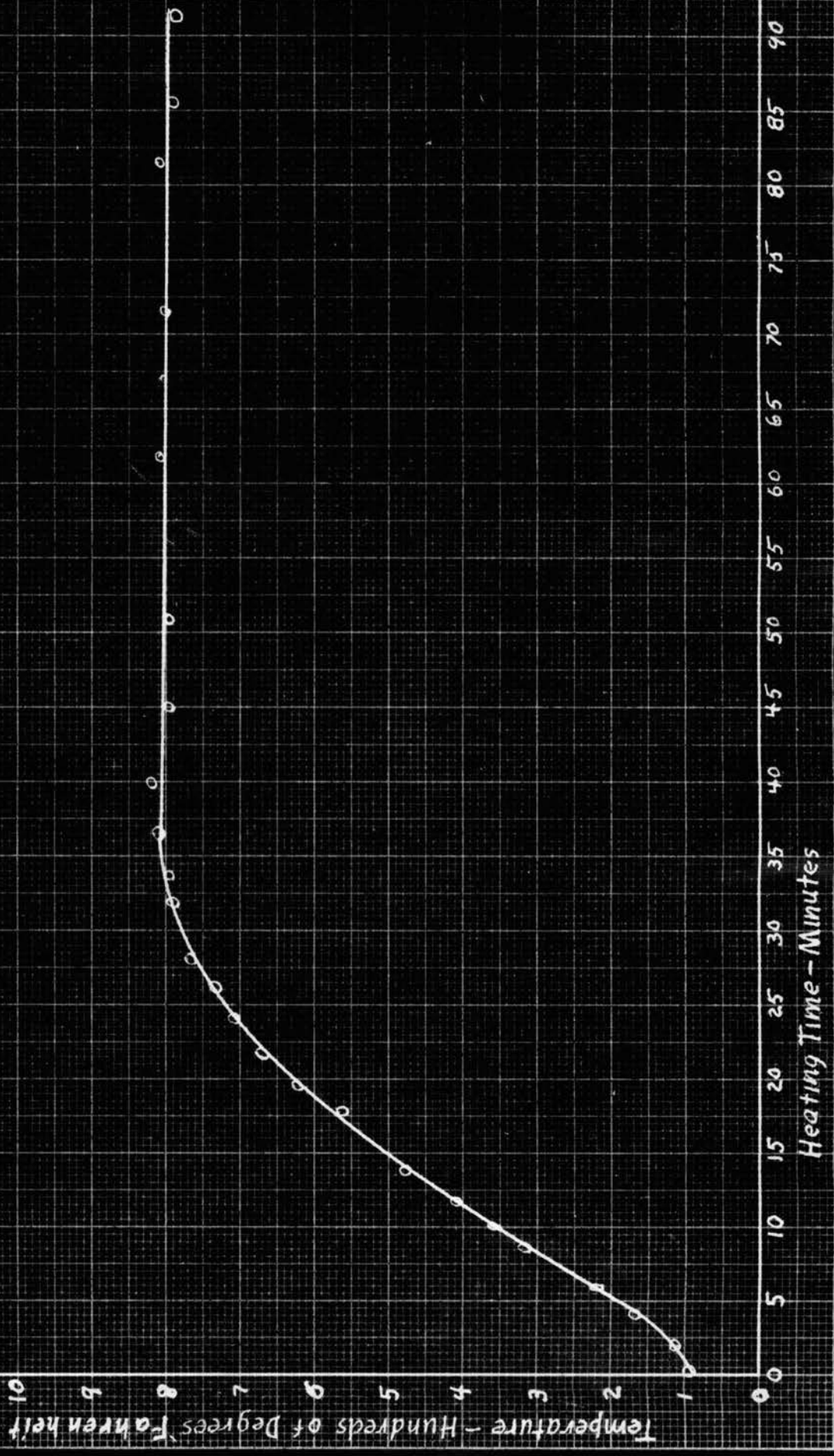


Table II

SCREEN ANALYSES AND MISCELLANEOUS DATA

Tyler Screen No.	35	65	100	150	-150	
	Percent Retained					
Raw Shale (Charge)	0.5	59.6	21.2	14.1	4.6	100.0
Run # 7B Discharge	0.7	62.4	19.7	13.1	4.3	100.2
Run # 1B Discharge	0.5	62.5	21.4	11.8	3.6	99.8
Run # 2B Discharge	0.6	60.9	18.6	13.7	5.9	99.7
Run # 3B Discharge	0.5	60.6	19.5	13.2	6.2	100.0
Run # 4B Discharge	0.4	58.9	21.0	13.5	6.2	100.0
Run # 5B Discharge	0.7	61.9	20.4	11.7	5.4	100.1
Run # 8B Discharge	0.6	60.2	19.3	13.3	6.5	99.9
Run # 6B Discharge	0.6	59.2	21.0	13.0	6.2	100.0
Run # 9B Discharge	1.1	60.2	19.7	13.0	5.8	99.8

Bulk density 75 #/cu.ft.

Shale bed density with .25 ft./sec. aeration 90°F 60 #/cu.ft.

Shale bed density with .44 ft./sec. aeration @ 800°F 20 #/cu.ft.

Carbonized shale has essentially the same bulk density as raw shale.

Raw shale 63.6% ash 0.3% H₂O
36.4% VCM

Fischer assay: 26 gallons oil and 5 gallons water per ton.

DISCUSSION

Since agglomeration within the bed did not occur, several flow patterns would merit investigation. In both of the retorts constructed, a horizontal outlet was brought out of the side for the gas take-off. This sharp turn and contraction, accompanied by some cooling, was disastrous in the case of a 1/4-inch pipe. The 3/4-inch pipe did not plug, but coke did accumulate on the lower wall. When more cooling and a 45 degree elbow were encountered, plugging did occur. This obstruction usually appeared to block the entire area, but a small aperture was sometimes apparent in the upper cross section. The flow of gas was never completely blocked in the line.

Even when two heated, external cyclones were used in series (the smaller one having only a 1/4-inch diameter inlet and an internal diameter of 1-inch), dust and mist were carried through and blocked subsequent points in the condensing system.

The problem is by no means insurmountable, but tedious qualitative and quantitative work will be necessary to determine whether the dust and vapor can be largely separated in the retort by internal cyclones or whether a tar mist is formed almost at once through the mechanism of polymerization.

There are various methods of dust and mist collection. Usually, the same principles are applied to either.

If we consider the probable mechanism of the cracking of kerogen (H:C atomic ratio of 1.6:1), some polymerization of the initial products can probably not be avoided. However, within the bed, a large surface area is available for the deposition of tars. Moreover, this deposition did not cause agglomeration under any of the conditions which were investigated. It is probable that, if a deeper bed were used, which would allow more time for the tar for-

mation to occur within the bed space, less tar forming materials would be carried over-head. Of course, this might defeat the chief object, that of obtaining liquid products. If this were the case, it would be better to employ a bed with a depth as shallow as possible and to quench the vapors with steam or recycle gas immediately above the bed. This would tend to halt vapor phase polymerizations by temperature lowering and dilution but would promote mechanical condensation.

Using a smooth tapered gas take-off, deposition of coke on the walls of the retort can be prevented. Cyclonic type mist collection or oil scrubbers could be employed to collect the resulting mist and smoke. The dust would then have to be removed by filtering, settling, washing or some similar method.

In the batch runs, it probably would have been possible to collect more of the oil, but the oil would not have been free of dust. This was not attempted because a previous course had already been planned.

An early error was made in attempting to work with mixtures of wide size ranges. While these materials fluidized readily at very low gas velocities, dusting was tremendous and bridging of solids was frequent. It was thought that heavy dusting would ensue when the shale became carbonized, even if fines were excluded, inasmuch as carbonized shale is more friable than raw shale. Also, as was stated in the introduction, a distinct advantage of a fluidized system would be in the utilization of fines. These statements are not necessarily contradictory. In a deep bed, under proper fluidizing conditions, fines could probably be handled advantageously.

A very uniform feed of closely sized material could be obtained from a vertical standpipe with a gently tapered outlet. Raw shale did not seem to flow as readily as carbonized shale with the same pinch clamp setting and essentially the same sizes of particles. The many difficulties encountered

with plugging and dusting should in no way be interpreted as being a unique characteristic of fluidized systems. Shale dust and tar occur in other systems in varying degrees. Stubborn emulsions are sometimes formed in the gas producer type of retort.

It is believed by the author that carbonized shale dust would not be as offensive as raw shale dust, and, that, with an adequate bed depth and proper distribution of feed, the dust could be largely separated internally on large scale operations. This method is employed to separate catalyst from vapor in catalytic cracking units. Oil scrubbing (baffle or centrifugal) could be used to remove dust and heavy tars at nominally high temperatures -- say 650° F. The dust-oil suspension could then be atomized into the retort. This would be practical only if the bulk of the fines could be handled by cyclones.

If we consider that only 18.4% of the shale is material capable of forming hydrocarbon, and that this is present as a very complex molecule containing an atomic ratio of hydrogen to carbon of about 1.6:1, a possible mechanism of cracking would be as follows:

First the material becomes moderately unstable in the region of 700° F, and there is a tendency for products having a greater thermal stability to be formed, i.e. those materials having a lower molecular weight or a lower hydrogen to carbon ratio.

However, the stability of kerogen itself is so great that its decomposition is very slow. When the temperature is further increased to 750° F, lower molecular weight compounds are formed.

In order for the kerogen to become more stable, its hydrogen: carbon ratio must decrease. By producing low molecular weight hydrocarbons with a higher (still low -- say di-olefins) hydrogen: carbon ratio and at the same time decrease both the molecular weight and hydrogen: carbon ratio in the

kerogen, temperature stability would be approached in several ways. The vapors would be partly unsaturated and tend to polymerize. The polymers now have a higher hydrogen: carbon ratio than the original kerogen and conceivably could have even a higher molecular weight. Therefore, they in turn would decompose and polymerize, resulting in tar deposited on the shale and materials of higher hydrogen: carbon ratio. Even at 750° F these mechanisms were relatively slow. However, the shale was blackened and one-third of the organic material was ultimately converted into volatile materials in an hour.

At 800° F the reaction proceeds much faster, and at 900° the reactions were substantially complete within the time interval required to reach 900° F. Further increasing the temperature would (and did) cause more decomposition, but only of the materials which were stable at 900° F. To be stable at 900°F, the residum would be very unsaturated and complex. Above 900° F only gasing occurs and probably this is due to the polymerized secondary products. That is, the rate of decomposition at 900° F was sufficient to convert all of the kerogen to thermally stable products which decompose very slowly at 900° F.

As the residum becomes more highly unsaturated and stable, the possibilities of forming products of a sufficient molecular size to be liquids and at the same time containing enough hydrogen to be even an aromatic or acetylene compound are negligible, simply because the hydrogen has already been depleted at the lower temperatures.

Since 650 grams of shale were carbonized within ten minutes (interval between 770 and 900° F) in a batch operation (Run 9B, Table XV), certainly at least that rate could be attained under continuous operation.

Therefore, at least 8.6 pounds of shale can be carbonized per hour in a 2-inch pipe which corresponds to 4.4 tons per day per square foot. The high temperature retorts which are used in Scotland handle only 0.7 tons per day

per square foot.

If a 36-foot diameter reactor were employed, 4500 tons per day could be carbonized. If the design coefficient of 150 Btu/hr./sq.ft. were used and fluidized combustion taking place at 1200° F on the outside of the vessel, the necessary area would be

$$\frac{4500 \times 350 \times 2000}{150 \times 300 \times 24} = 2900 \text{ sq. ft.}$$

or a bed height of 26 feet.

This would have commercial possibilities, if fines could be used. Crushing of the shale was relatively simple. Perhaps several smaller retorts could be advantageously employed on air classified fractions.

A logical retorting rate obtained from the data at 800° F (Runs 3B and 4B) would show that 650 grams are substantially retorted within an hour at this temperature. Since the thermal decomposition rates of petroleum practically doubles for every 10° C, the reaction rate at 900° F would be 32 times the reaction rate at 800° F (assuming the same reactions) and only 2 minutes would be required to retort 650 grams at 900° F. Thus, the rate would more probably be 22 tons per day per square foot of cross section. Unfortunately, it was not determined whether or not such a rate is permissible, but it is unlikely that agglomeration within the bed would have occurred even if the rate of retorting had been more rapid.

RECOMMENDATIONS

It is recommended that the present apparatus be used for studying mixtures of coking and non-coking shales and coals. Preliminary tests should be made in a crucible to determine what mixtures will agglomerate when agitated. Complete oil recovery should be attempted.

It is further recommended that detailed flow characteristics of shale be investigated, using glass apparatus.

The possibility of merely blowing shale upward through heated tubes into heated cyclones should be investigated as a means of utilizing fines.

It is recommended that the following corrections be incorporated in the design of a continuous retort:

- (1) The reaction heat should be supplied through a short section known to be well below the bed level. It is virtually impossible to overheat the wall in contact with the bed. Alundum cores should be used in lieu of asbestos.
- (2) A gas distribution grid should be used.
- (3) The outside cross sectional area of the bottom solids draw-off should be large in relation to the reactor - say one-quarter of the cross sectional area. This would serve as a convenient anti-slug section.
- (4) At least three feet should be allowed for solids disengaging space and a deep bed should be used.
- (5) Recording instruments should be used on the project.
- (6) Steam should be employed for aeration. This would necessitate pre-heating the feed if a bottom feed is used. Sufficient pressure should be available for constant gas flow. Pulse chambers should be avoided.
- (7) Dust and oil separation should not be attempted at first. Large piping with smooth turns should be used in the gas take-off. The thermocouple shield for measuring internal temperatures should be supported by the distribution grid and led down through the feed inlet. This would necessitate an annular feed. At least prelimin-

ary flow experiments should be made, before designing a reactor.

APPENDIX

STRATHMORE PARCHMENT

100 PARAG U.S.A.

PARCHMENT

U.S.A.

NOTE: Explanation of symbols used in Tables
III, IV, and V.

- P - pressure below feed inlet, centimeters of mercury.
- P - pressure drop across reactor, centimeters of mercury.
- T₁ - bed temperature $5\frac{1}{2}$ inches above bottom flange °F.
- T₄ - outside wall temperature 18 inches above bottom
flange, °F.
- T₅ - outside wall temperature 10 inches above bottom
flange, °F.
- T₆ - outside wall temperature 2 inches above bottom
flange, °F.
- Q - Gas flow rate in cubic ft./min. at P and initial T.

Table III

Log of Continuous Run E

The purpose of this run was to obtain a sample of carbonized shale with which to charge subsequent runs.

Take-off from bottom of first cyclone being vented to atmosphere.

670 grams solids from previous runs to be charged.

Time Minutes	Q	P	P	T ₁	T ₄	T ₅	T ₆
		0	0	85	85	85	85
Feed choked above solids inlet when attempt to reduce velocity was made.							
0	0.71	three minutes for feed (about 500 grams to enter), remaining charge in about one minute.					
8½	0.51	3-4	4-4½				
12		3	4½	100	180	180	160
14				150	300	300	230
15		3	4½	230	390	370	290
18		3-4	4½	310	490	490	350
20				350	visible gas		
21	0.52	3-4	5	400	580	540	430
23				415	600	560	460
30				500	650	630	530
31	0.52	3-5	5	520	670	650	560
35	0.52			gas leaving white (opaque)			
				590	740	700	610
38				620	760	730	650
40				670	800	780	690
41		3-4	5	680-90	820	800	710
45				copious white discharge			
				730	860	840	760
47	0.54	3-4	5	770	880	870	780
49		rapid evolution		760-70	900	880	790
53				800	950	920	830
55				830	990	950	860
60		2½-3	5	880	1030	980	900
				gas evolution subsided			
63	0.43	1½-2	11	900	1060	1000	920

Gas and heat off

Pressure dropping, charge dropping nicely

Bottom discharge uniformly black

Side arm collection speckled

Very heavy oil collected in ¾" T

½" pipe lined with light oil

Table IV

Log of Continuous Run II

630 Grams initial charge
Vented to atmosphere

Time Minutes	Q	P	P	T ₁	T ₄	T ₅	T ₆
0		3	3-4	90	90	90	90
1		all heaters on					
2				120	200	210	190
3	0.69			160	280	280	230
5		3	4	280	450	400	330
8				420	600	500	400
11				540	visible discharge		
13				610	800	620	520
16				730	900	700	600
19		2½-3	4	790	980	750	660
21		heater off					
31				830	1030	780	670
34				850	1040	800	700
37				890	1060	810	720
41		adding raw shale		100 grams in standpipe			
51				910			
55	0.31			920			
58		isothermal at 920		920	discharge very opaque		
60		all shale in		910			
62				920			
64		2½-3	4	930	1130	900	840
68		discharge still opaque		970	adding more shale 10 grms/min.		
72				1000	1170	940	870
76				970	1200	950	900
81				970	1200	960	900
83		all shale (100 grms) in		970	1200	970	900
87				1000			
88		adding more shale, shale going in about 20 grms/min.					
92			3	1000	1220	1000	930
95	0.25			1000	1230	1000	940
93	100 grms	3	4	1000	1220	1020	960
		more in, total 300 grms., practically no discharge, shutting down					

Charge dropping nicely about 3 minutes. Side arm collection negligible. Bottom sample taken (draw off sample not significant because of large (about 100 grms.) amount blown off when heated. Sample taken for screen analysis. (490 grams in retort, bottom discharge) (300 grms in take-off flask). Vent pipe blocked with tar and shale.

Table V

Log of Continuous Run I

Charge 460 grams from Run G

Time Minutes	Q	P	P	T ₁	T ₄	T ₅	T ₆
0		2	3	75	80	80	80
4	all heaters on						
5				80	200	210	170
6				150			
8	0.36	2	3	290	430	510	300
1				500	570	670	380
6				820	810	860	500
10	one heater off, adding raw shale						
11	(shale blew out of standpipe, glass tube in condensing system broken, replaced with rubber)						
3				920	1070	1140	640
5	heated separator burning with awful odor (not oil shale)						
12	Heater off, gas off, pipe insulation replaced						
20		2	3	620	710	620	450
23	third heater on @ 4						
23 $\frac{1}{2}$				800	940	800	
28				830	1060	920	670
29 $\frac{1}{2}$	insulation burning again, heaters off, continue with insulation off						
9 $\frac{1}{2}$				810	950	780	600
33	all heaters on, opaque at 930, all condensers leaking						
38				970	1170	1030	800
39	adding raw shale, discharge immediately yellow. Shale in about 20 grms/min. Black tar in air condenser						
				1000	1220	960	840
33	Sample #1 taken, oil oozing out everywhere in condensing system						
38	Sample #2 taken at 9; back pressure building up						
39	gas off						
				1030	1200	1020	

Heavy brown oil in air condenser flask (flask ran bright yellow). Seems to be practically nothin in ice water flasks, but tar leaking out both corks. Bottoms are dirty from dust and film of oil, about $\frac{1}{2}$ cc liquid in each, very foul odor. First dry ice bath lined with orange crystals on bottom, yellow crystals on sides. Outlet plugged with brown oil and orange crystals (not cause of shut down, but evidently cause of condenser leaks) - unbearable odor. Orange crystals disappeared when inspecting, leaving behind etched structure of solid material (dark). Appeared to be tar later.

Second dry ice flask, pale lemon color on sides, same general odor, grayish deposit on bottom. Everything but a few specks of tar (coke) evaporated.

All flasks contained dust.

Small quantities of liquid in ice water flasks non-combustible water.

NOTE: To be referred to in connection
with Table VI through XV.

All of the following runs were made with Nitrogen line pressure at 26 psig. and a flowmeter reading of 4.5 inches of water (.31 cu.ft./min.). These readings were frequently noted and never varied. The charge was 650 grams of raw shale in each case except Run IB (625 grams). The actual discharge weight of this run was corrected to correspond to a 650 gram charge. The gauge pressure at the bottom of the retort was always between 1 and $1\frac{1}{2}$ inches of mercury except in one case when the outlet became badly plugged (Run 6B). Plugging within the bed never occurred as was indicated by oscillation of the manometer column.

Symbols

- T_1 ——— Bed temperature six inches above the top of the cone (12 inches above cone in shake down run).
- T_2 ——— Outside wall temperature 40 inches above top of cone.
- T_3 ——— Outside wall temperature 12 inches above top of cone (between upper and lower heater windings).
- T_4 ——— Outside wall temperature of $1/8$ " pipe (1 inch below the bottom of the cone).

All temperatures are in degrees Fahrenheit.

The time was recorded as minutes: seconds after heaters were turned on.

Table VI

Shake Down Run

Time	T ₁	T ₂	T ₃	T ₄	Time
0	90	90	90	90	0 : 50
3 : 0	120	160	170	125	3 : 45
6 : 0	180	240	240	155	6 : 40
8 : 0	240	290	300	180	8 : 50
10 : 00	300	335	360	200	0 : 55
2 : 00	370	390	410	225	2 : 50 gas faintly visible
4 : 00	435	435	460	250	4 : 53 characteristic odor
7 : 00	530	500	540	275	7 : 40
10 : 00	600	550	600	300	0 : 46
2 : 00	630	580	650	320	2 : 48
5 : 00	690	630	705	340	5 : 55
7 : 30	745	670	760	355	8 : 20 gas yellow
9 : 30	780	700	790	370	0 : 23
1 : 30	810	740	820	380	2 : 15
5 : 30	850	790	875	400	6 : 00 tar dripping
7 : 00	900	820	900	420	7 : 42
9 : 00	920	840	930	430	9 : 38 copious gas, tar no longer dripping
10 : 00		shutting down	heat off		
2 : 30	960	850	950	430	3 : 10

520 grams discharge

Thermocouple shield was blackened near the top and bottom four inches - gray over rest of length. A few particles were loosely adjerent to the shield and spiders.

Table VII

Log of Run 1B

To be terminated at 750° F.

Time	T ₁	T ₂	T ₃	T ₄	Time
0	130	130	130	130	0 : 50
2 : 00	140	180	175	160	2 : 35
4 : 00	170	150	230	180	4 : 40
		T C plug loose			
7 : 00	230	150	300	220	7 : 30 dusting on vent pipe
10 : 00	310	300	370	240	10 : 35
12 : 00	350	440	410	250	2 : 45 visible gas
4 : 30	420	500	450	270	5 : 20
6 : 00	435	520	480		
8 : 00	490	560	530	300	
20 : 00	530	600	570	320	0 : 35
2 : 00	590	640	620	350	2 : 45
4 : 00	620	670	650	360	4 : 40
6 : 00	670	700	700	375	6 : 35
7 : 00	700	heaters off			
8 : 00	720	730	735	390	8 : 45
9 : 00	735	730	735	390	
10 : 00	735				
11 : 00	740	720	730	390	
12 : 00	gas off, discharging (solids fuming slightly, do not appear to be black)				
4 : 30	730	700	720	580	
5 : 30	all discharged				

Discharge brown in color (625 grams)

2 grams fines (including some oil) in offtake.

Table VIII

Log of Run 2B

To be held at 750° F for one hour

Time	T ₁	T ₂	T ₃	T ₄	Time	
0	90	90	90	85		
2	110	145	140	120	2 : 40	
4	170	210	200	150	4 : 40	
6	240	270	270	180	6 : 40	
8	320	310	320	210	8 : 45	gas visible (faint largely dust)
10	380	350	380	240	10 : 45	
2	450	410	440	250		characteristic odor
4	490	460	480	270		
6	525	510	520	275	8 : 50	
8	550	550	550	290	8 : 45	
20	580	590	580	300	20 : 40	
2	600	630	615	310		
4	630	680	640	320		
6	660	720	670	330		gas white
8	680	740	680	380		
30	700	760	700	340		
2	710	770	710	350		
4	720	770	720	350		
6	730	770	740	370		
8	750	770	750	370		
40	760	760	760	370		
3	760	755	760	370		gas yellow
5	760	750	760	370		
8	750	745	750	370		
50	750	740	750	370		
2	750	740	750	370		
6	750	745	750	370		
60	740	760	740	360		
70	760	760	760	380		
80	755	750	755	380		
90	745	740	750	380		discharged
98	755	740	760	380		

620 max T₄ 650 Thermom. reading in flask

Coke in 3/4 inch pipe was sticky (not hard), putty-like consistency.
Negligible oil collected
576 grams discharge.

Table IX

Log of Run 3B

To be heated to 800° F and discharged

Time	T ₁	T ₂	T ₃	T ₄	
0	90	90	90	90	
2	110	140	150	120	top heater reduced
4	170	195	200	140	
6	230	220	240	170	
8	320	270	320	200	Attempting to control heaters
10	370	340	370	220	
2	420	380	420	235	
4	460	440	460	250	
6	480	480	490	250	visible gas
8	530	530	530	270	
20	565	570	570	290	
2	600	610	610	300	
4	640	645	650	320	bouncing
6	700	680	700	340	
8	750	710	740	360	
9	770	heater off			
30	785	740	770	360	
2	770	780	790	360	yellow discharge, heater back on
4	790	805	810	370	
5	810	dumping (discharge fuming rapidly)			

7 grams of a very light oil (visual inspection) having olefinic odor (not found in previous batch run oils) essentially the same odor as was noticed in dry ice flasks in continuous run.

571 grams discharged Soft mud (little) in coking region (discharge)
 Apparent bed line 23" above bottom 17" up on T shield

Table X

Log of Run 4B

To be heated to 800° F and held for one hour

Time	T ₁	T ₂	T ₃	T ₄	
0	90	90	90	90	
2	100	130	130	110	
4	160	160	190	130	gas faintly visible
6	220	260	250	150	T ₁ 250 at end
9	320	350	350	190	
10	360	380	390	210	
2	410	410	410	210	characteristic odor
4	480	460	480	235	
6	525	500	520	250	
8	570	540	570	275	gas white
20	620	580	620	290	
2	670	610	660	300	
4	700	650	700	320	
6	730	690	730	330	
8	770	720	760	340	heat off awhile copious gas yellow discharge
30	780	750	780	340	
2	800	780	800	340	
4	800	810	800	350	
7	810	820	820	350	
40	820	830	830	360	
45	800	840	810	360	
52	790	810	800	360	discharge much lighter (white) in color, still dense
62	805	790	805	370	
72	810	790	810	370	practically no discharge (faint white)
82	810	790	820	370	
86	800	800	800	360	
92	790	810	800	365	discharge completely black, no smoking. Discharged in 2½ min.

539.5 grams discharge 15 grams oil 10 grams mud

Table XILog of Run 5B

To be heated to 900° F

Time	T ₁	T ₂	T ₃	T ₄	
0	100	100	100	100	
2	110	120	130	120	
4	170	160	180	140	very faintly visible
6	250	200	250	170	
8	330	250	300	190	
10	360	280	340	200	
2	410	310	380	220	
4	450	340	420	230	
6	470	370	440	230	
8	480	420	470	235	
20	500	465	490	240	
2	510	500	510	250	
4	530	550	540	260	
6	560	590	570	270	
8	600	630	600	290	
30	650	660	650	310	
2	700	670	690	320	
4	740	690	730	340	
6	775	730	770	350	copious yellow gas
8	810	760	800	360	
40	820	800	820	370	
2	840	820	840	380	
4	860	850	860	390	
6	880	880	880	390	
8	900	900	900	400	vapor becoming white

538 grams solid discharge
 more oil than previously collected
 very fluid 23 grams oil 15 grams mud

8:45 discharging
 9:55 smoking slightly
 all discharged

Table XII

Log of Run 6B

To be held at 900° F for one hour

Time	T ₁	T ₂	T ₃	T ₄	P _r	
0	90	90	90	90	1 - 1/8	
2	110	140	140	110	"	
5	190	225	210	140	"	
6	220	255	240	150	"	
8		310	300	180	"	
10		390	400	210	"	
4	480	430	460	230	"	visible gas
6	510	470	490	240	"	
8	540	510	530	250	"	
20	580	550	570	270	"	
2	610	585	610	280	"	
4	640	620	630	290	"	
6	670	660	670	300	"	
8	690	690	690	310	"	
30	710	720	720	320	"	
2	750	750	750	330	"	gas becoming yellow
4	790	790	790	350	"	
6	820	820	820	360	"	
8	850	830	840	360	"	
40	860	850	850	370	"	
2	870	850	860	370	"	
4	875	860	880		"	gas white, thinning
6	900	880	905	400	"	
9	940	910	940	400	1 - 3/8	heaters off at 8 on at 3 outlet partially plugged
56	910	900	910	390	1 - 5/8	still jiggling
66	910	910	920	395	"	
76	900	920	910	390	"	
86	900	940	910	390	"	
96	900	900	900	400	1 - 1/2	
106	900	900	900	400	"	solid discharge not smok- ing discharged in 2 min.

3/4" pipe and 45° elbow completely blocked
 525 grams discharge
 30 grams coke (mud) 22 grams oil

Table XIII

Log of Run 7B

To be held at 550° F for one hour

Time	T ₁	T ₂	T ₃	T ₄	
0	90	90	90	90	
2	120	150	140	120	gas visible
4	170	210	200	140	
6	240	270	270	160	
8	330	340	340	190	both heaters still on full
10	400	400	400	215	
3	500	470	490	250	bottom heater off
4		top heater reduced			bottom one reduced
5	540	500	530	250	
6	550	500	540	250	
8	550	500	550	260	
20	550	500	550	260	
26	550	530	555	260	
36	550	560	555	270	
46	550	560	560	270	
56	550	550	550	270	
66	550	560	550	270	
76	550	550	550	270	

no smoke or fume in discharge 2 minutes to discharge

608 grams discharged 18 grams held up in retort (as free flowing material)

6 grams agglomerated powder (enough to block gas outlet)

no oil

Table XIV

Log of Run 8B

To be held at 900° F for one hour

Time	T ₁	T ₂	T ₃	T ₄	
0	95	95	95	90	
2	110	140	140	110	
4	160	200	190	140	
10	350	350	355	200	
14	Shut down to repair N ₂ line down 6 min. Shale not discolored, but firing slightly (it was noted that thermocouple shield was freed as usual, but shale was definitely raw) Dumped and recharged				
20	430	380	420	230	
3	450	430	470	260	bottom heater reduced
6	520	490	520	270	
8	560	540	560	280	
30	580	580	590	290	
2	610	620	610	300	
4	640	650	650	310	
6	670	680	680	320	
8	710	705	710	340	gas very dense white
40	750	740	750	350	both heaters on full
2	790	770	790	365	upper heater reduced full rheo.
4	820	810	810	370	adjusting both heaters
6	830	820	820	370	
9	830	830	830	380	
52	850	850	855	390	
3	870				gas whitish yellow
4	870	860	870	390	
6	880	870	880	400	
8	890	870	890	400	discharge definitely white
60	890	870	880	400	
68	900	900	900	400	
78	900	900	900	405	
88	900	900	900	405	
98	900	900	900	405	
108	890	900	900	405	
118	900	900	900	410	

1 - 2/3 min. discharge

528 grams discharge

22 grams oil

18 grams mud

Table XV

Log of Run 9B

To be held at 1100° F for one hour

Time	T ₁	T ₂	T ₃	T ₄	
0	90	90	85	85	
2	100	140	140	120	
4	160	190	190	130	
7	260	280	280	170	
8	290	310	310	180	
10	350	350	350	200	no control on heaters yet
2	430	410	430	220	lower heater reduced
4	475	460	470	240	back on full
6	530	500	520	250	
8	570	540	560	270	reduced lower heater increasing
20	610	580	600	275	
2	620	620	620	280	
4	635	645	640	290	bottom heater on full
6	660	675	675	300	copious white gas
8	700	710	700	320	
30	740	740	740	330	gas yellowish
2	780	770	780	340	
4	810	800	810	350	gas dense, yellow
6	850	830	850	370	
8	880	860	880	380	copious; yellow
40	920	880	910	390	brown
2	950	910	940	400	thinning
4	990	940	960	410	bouncing as if plugged
6	1010	970	1000	420	heater controlled
8	1030	990	1010	420	
50	1030	1000	1020	430	
2	1040	1020	1030	435	
4	1050	1030	1050	440	gas very dense white after having subsided
6	1065	1050	1060	440	
8	1080	1070	1080	450	
60	1090	1080	1090	450	
62	1100	1100	1100	460	
72	1130	1110	1120	470	
82	1070	1090	1070	460	
92	1100	1100	1100	470	
102	1110	1100	1100	470	
112	1100	1100	1100	480	
122	1100	1100	1100	480	dumped 1 - 2/3 min.

512 grams discharge
22 grams oil

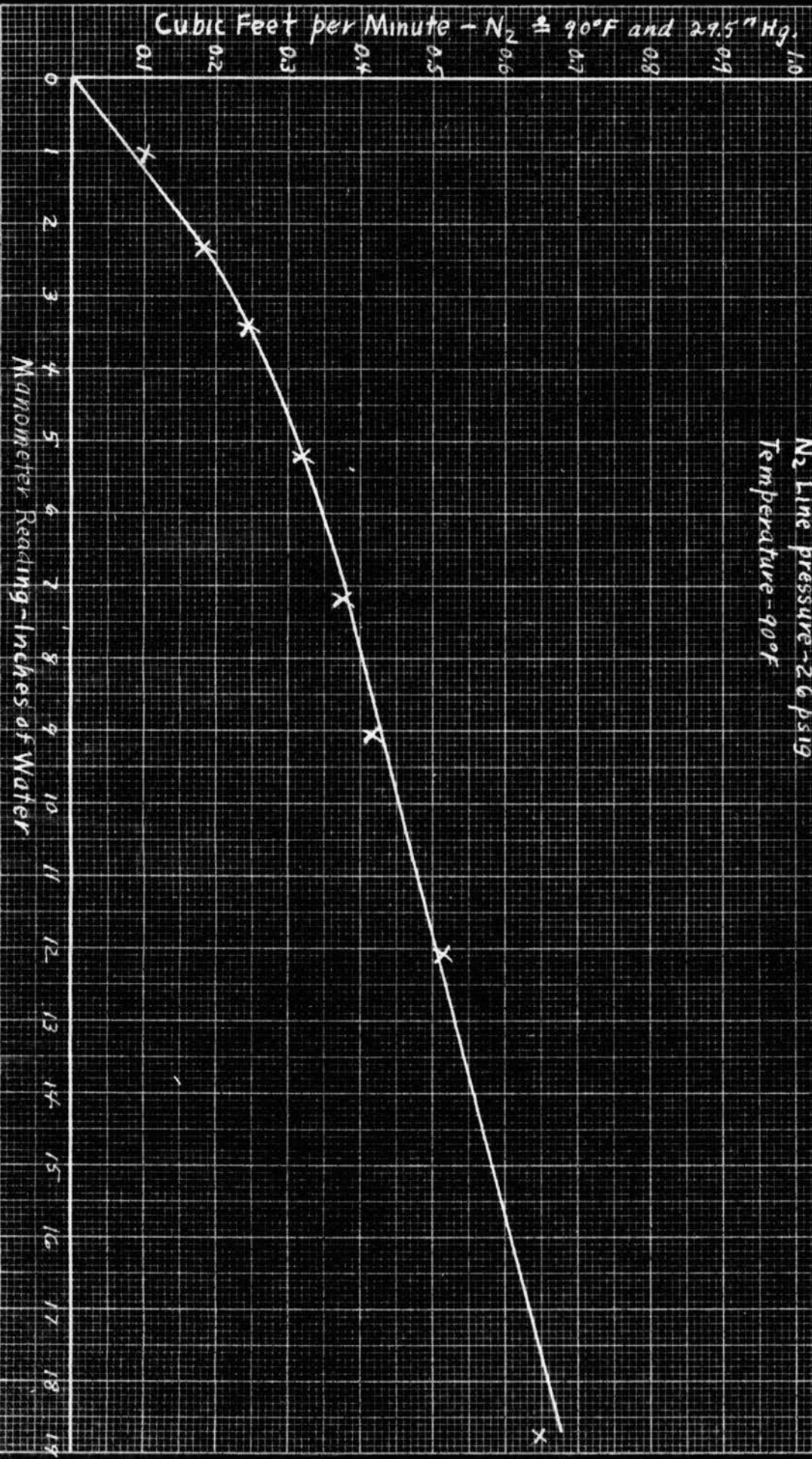
SAMPLE CALCULATIONS

Rum 5B Used in preparing Table I

Item #5	% Total overhead	$\frac{\text{Wt. Charged} - \text{Wt. Discharged}}{\text{Wt. Charged}} \times 100$ $\frac{650 - 538}{650} \times 100 = 17.2\%$
Item #7	% Ash	$\frac{650 \times .636 - 538 \times .734}{650} \times 100 = 2.8\%$
Item #6	% VCM overhead	$17.2 - \text{per cent ash} = 17.2 - 2.8 = 14.4\%$
Item #8	% oil collected	$\frac{23}{650} \times 100 = 3.5\%$
Item #9	% mud	$\frac{15}{650} \times 100 = 3\%$
Item #11	% VCM remaining	$\frac{\text{VCM}_{\text{dscg.}} \times \text{Ash}_{\text{raw shale}}}{\text{Ash}_{\text{dscg.}}} = \frac{26.6 \times 63.6}{73.4} = 23.0\%$
Item #10	% VCM distilled	$\text{VCM}_{\text{raw shale}} - \text{Item \#11}$ $36.4 - 23.0 = 13.4$
Item #12	% CO ₂ remaining	$\frac{121 \text{ ml.} \times 44 \times 63.6 \times 100 \times 492 \times 29}{22400 \times 73.4 \times 550 \times 30} = 18\%$
Item #13	% HC remaining	$23 - 18 = 5$

FIGURE 5.
FLOWMETER CALIBRATION

N₂ Line pressure - 26 psig
Temperature - 90°F



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Typist